Ontario

Practices for the Collection and Handling Of Drinking-Water Samples

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1.0 Introduction

To ensure the provision of safe drinking water to the citizens of Ontario, regulatory requirements under the *Safe Drinking Water Act* govern the sampling and testing of water provided by municipal and non-municipal communal water systems. The purpose of this document is to provide guidance for the collection, labelling, storage, transportation and chain of custody of all drinking-water samples that fall under the Drinking-Water Systems Regulation (Ontario Regulation 170/03). These practices may be used by treatment plant owners/operators sampling to meet Ontario's environmental regulatory and approval requirements, and by provincial officers sampling to verify the integrity of a drinking-water system's self-monitoring information, or sampling in response to adverse water quality notifications. The licensed drinking water laboratory may also use these procedures as a guide for the safe handling and storage of drinking water samples.

These practices provide the minimum level of quality assurance necessary to ensure that the samples analysed continue to accurately reflect the quality of the raw, treated and distributed water supply. They comprise "front-end" quality assurance activities and are intended to supplement the analytical method quality assurance and control activities already in place. It is recognised that laboratories and drinking-water systems may have their own standard operating procedures for the collection and handling of drinking-water samples. Where they exist, these procedures must incorporate best practices for ensuring the integrity of the sample.

1.1 Limitations

This document is intended to apply only to grab samples that are collected and transported to an off-site accredited laboratory for analysis. Operational checks of the treatment process, which include the continuous in-line monitoring for parameters such as pH, turbidity, chlorine residual and fluoride, are beyond the scope of this document. It is expected that drinking-water system operators can apply many of the quality assurance principles discussed here to the collection and analysis of discrete grab samples on-site by the operators for routine, non-regulated "process" parameters such as colour, residual aluminum, fluoride, iron, manganese, alkalinity and sodium.

1.2 Why Have Standard Sample Collection and Handling Protocols?

Chain-of-custody records and standard protocols for sample collection, labelling storage and transportation to the laboratory help to ensure the integrity of the analytical data. These protocols are equally applicable to samples taken by drinking-water system owners/operators, provincial operators and laboratory staff. Standard protocols and best practices facilitate uniform compliance inspection program delivery

throughout the province, and ensure the collection and monitoring of similar information for each sample. Such procedures also help maintain the integrity of the information stored in the provincial Drinking Water Information System (DWIS) database. This corporate database can then be used confidently by other branches of the ministry and other jurisdictions. The data can also be used in the Ministry of the Environment's Drinking Water Surveillance Program (DWSP) to identify drinking-water systems that have specific and unique optimisation challenges.

Audit samples, taken to verify a drinking-water system's self-monitoring data and procedures, are more reliable when water system owner/operators and Provincial Officers use standardised sample collection and handling procedures. Accredited drinking-water analytical methods can only produce reliable, high quality data when laboratory and field personnel use sample collection and handling best practices consistently.

2.0 Representative Samples And Representative Data

The water sampling and analyses required by the Drinking-Water Systems Regulation are intended to ensure the provision of safe drinking water. As such, sampling and analytical activities must be carried out in a manner that produces data that accurately describes and represents the quality of the water in the supply system.

A *representative* sample is one that reflects the same characteristics as, and can be considered an accurate subset of the material being measured. Representative samples taken in a similar manner at the same time and location have an equal probability of yielding the same result. The location, time and method of sample collection must adequately define and isolate the material of interest or concern. For example, when selecting the time and location of distribution system sampling, consideration must be given to peak usage periods and the isolation of the effects of reservoir or elevated tank storage, dead ends in the system, the extremities of the distribution system and residential plumbing. Simply put, the sampler must be cognisant of the conditions that the material sampled represents. Sampling points must be selected to address the intent of monitoring outlined in the Drinking-Water Systems Regulation. The choice of sample type (i.e. grab samples, composite samples or continuous in-line sampling) will depend on certain characteristics such as average, maximum or minimum concentrations of a contaminant. As well, the sample type selected must be fit for purpose so that the data gathered meets the monitoring objectives.

The integrity of the target analyte of interest must be maintained by taking steps to ensure that the physical, chemical and biological characteristics of the sample are not compromised. Sample collection and handling procedures are the key steps in ensuring that the sample remains representative. Temperature control and chemical

preservation are two measures that may be taken to stabilise a sample after collection. The sample should also be protected from contamination by extraneous materials. Best practices must also be followed for recording sample information, maintaining chain-of-custody, and for sample labelling, transportation and storage procedures. In summary, a drinking-water sample arriving at the laboratory must be traceable to its origin, and time and date of collection, and must continue to accurately reflect the concentration of target analyte at the location and time of sampling.

Storage duration is also a consideration; the lag time between sample collection and analysis should be geared towards minimising changes in analyte concentration. Testing must be performed in a manner and by a method with sufficient sensitivity, precision and accuracy to ensure that the result can be used confidently for comparison with the Ontario Drinking-Water Quality Standards (Ontario Regulation 169/03). Acceptable methods for drinking water testing are listed in the *Protocol for Accepted Drinking Water Testing Methods*, June, 2003 (as amended from time to time).

3.0 Sampling

The location and manner in which a sample is collected and handled in the field is the first step to ensuring representative and reliable analytical data. This document recommends practices that the Ministry of the Environment, the Ontario Clean Water Agency and other leading jurisdictions have found to be the minimum requirements to ensuring a valid sample. However the document is not prescriptive. The sample handler or analyst may incorporate additional quality assurance activities into sampling designs and procedures, which will further improve the certainty of the analytical data. In specific cases, local conditions (geology, industry, etc.) will necessitate additional sampling and analysis over and above that required by regulation. Additional requirements may be listed in an approval issued to the drinking-water system, an order (including an Ontario Water Resources Act order) or another directive. Best practices should also be followed for all samples collected to comply with approval and other control document requirements.

3.1 Sample Type

In most environmental sampling situations, two types of samples are generally considered: *composite* samples and *grab* samples.

Composite samples are most appropriate in situations where the sampler is seeking to obtain information on the average value of a system in which a high degree of variability in the characteristics of the system or process being sampled is expected over time. An example of such a system is an industrial waste stream.

Grab samples consist of discrete samples collected over a period of time, generally not exceeding 15 minutes. *Grab* samples represent the characteristics of the water sampled at a particular point in time. Sampling at the same point at a given frequency will allow the identification of trends through time and can provide a measure of variability over the long term. Grab sampling methods are used to fulfil the requirements of the Drinking-Water Systems Regulation. Sampling discussions in this document are restricted to *grab* samples. In addition to *grab* samples, the monitoring of treatment efficiency and effectiveness at large water treatment facilities requires continuous process control. This is achieved through the continuous measurement of the effectiveness of the coagulation/sedimentation/filtration and disinfection processes by in-line measurements of parameters such as total and free chlorine residual and turbidity. Best practices related to these types of sampling and analysis is beyond the scope of this document.

3.2 Sampling Design

Environmental sampling strategies and designs generally fall into two groups: *directive* or *probabilistic*. Directive sampling strategies are based on instructions that are laid out in regulations, permits, approvals and other authorising documents. This approach is used when there is an understanding of the system and its anticipated characteristics. In this situation, legislation or control documents are used to specify sampling locations and frequency of sampling. Sampling as required by the Drinking-Water Systems Regulation is an example of directive sampling.

A *probabilistic* approach would be used in environmental investigations designed to determine the source and/or extent of possible contamination of an area. This approach relies on field experience, historical documentation and knowledge of the behaviour of the contaminant under specific environmental conditions.

3.3 Sampling Location

The Drinking-Water Systems Regulation requires the collection and testing of raw water, treated water and distribution system samples. The sampling locations must be carefully chosen to ensure that a sample accurately represents the quality of the water being sampled. As per the *Terms of Reference: Engineer's Report for Waterworks* (January 2001), the Engineer is responsible for recommending a site-specific monitoring program for the supply/treatment/storage works and the distribution system, in accordance with the Drinking-Water Quality Standards Regulation (O. Reg. 169/03) and the Drinking-Water Systems Regulation (O. Reg. 170/03).

3.3.1 Raw Water:

Raw water refers to the source water for the water supply system. Its characterisation is necessary to decide on treatment requirements. Changes to the temperature, pH,

alkalinity, colour, turbidity and biological quality of the source water will affect the efficiency of, and may necessitate alterations to, the treatment process. Raw water characterisation with respect to all parameters listed in the Ontario Drinking-Water Quality Standards Regulation and the Drinking- Water Systems Regulation is required in the preparation of the Engineers' Report. Frequent raw water monitoring for microbiological contamination is also required under the Drinking-Water Systems Regulation.

All raw water samples should be collected prior to any treatment process. For ground water systems using more than one well supply, grab samples for microbiological testing are required from each well on the system. If many wells are used and the water is blended at or before the high lift pumps, samples of the raw water from each well before blending should be taken. Sample collection assumes the availability of in-line plumbing, including the presence of a tap/spigot prior to any treatment process. If this is not the case, it may be necessary to shut down the pump and open the sanitary seal. Ideally, samples should be collected from a tap located as close as possible to the well. Usually a tap in the pump house is used. Sometimes a continuously running tap is present and provides a fresh representative sample of the raw water. The waste from the tap, however, should not be allowed to drain back into the well. The raw water sample must be taken preferably before the water enters any storage/pressure tank and definitely before any treatment. If samples are taken after storage units, the unit should be purged to allow a complete exchange of water. If samples are taken before a storage unit, taps/spigots located after the storage tank should be opened to prevent back flow from the storage unit. If it is necessary to turn off the disinfection system to obtain a raw water sample, the resulting water must be wasted and not allowed to enter the distribution system.

In surface water systems, it can be difficult to collect samples at an intake that is located at a great distance from shore. Near shore samples are not recommended as they are subject to increased turbidity, algal blooms and bacteria and do not accurately represent the water quality at the intake. Moreover, high, intermediate and low level intakes mean that different levels in the water body can be used for treatment simultaneously or during different periods of the year. For these reasons, samples are generally taken after screening, pre-sedimentation, wet well storage and low lift pumping to the treatment facility. These samples will reflect any changes in source water quality resulting from these activities. To adequately characterise the raw water source it is recommended to take the sample prior to any aeration/oxidation and pre-chlorination which is performed. At some locations, however, it is necessary to pre-chlorinate at the intake for zebra mussel control. During certain months of the year it may not be possible to sample unchlorinated raw water at these locations. In these cases, the installation of a separate intake line with tap at the plant is advised to allow the collection of samples that have not received treatment. If multiple surface

source waters or a blend of ground and surface sources are used, each raw water source should be sampled separately prior to blending.

3.3.2 Treated Water:

Treated water refers to all water which has undergone one or more treatment processes such as chemically assisted filtration, iron and manganese sequestering, primary disinfection, corrosion control, softening, fluoridation etc. Treated-water sampling locations must be selected to ensure that the samples represent the treated water after all treatment processes are complete. The sampling location must be at the point of entry of the water to the distribution system, after the minimum disinfection contact time and before the first consumer. Samples must be taken prior to standpipe, elevated tank or reservoir storage.

3.3.3 Distribution System Water:

The term distribution system refers to the entire network of storage tanks, reservoirs, standpipes, pumping stations, pumps, valves, metres and service pipes that deliver the treated water leaving the drinking-water system to consumers. Sampling of the distribution system is mandatory under the Drinking-Water Systems Regulation and the required number of samples collected depends on the size of the population served. The selected sampling locations should be points significantly beyond the point of entry to the distribution system. These locations should represent and cover the distribution system, especially locations where the degradation of water quality and disinfection residual are possible and the formation of disinfection by-products is likely. Sampling locations should address elevated storage tanks within the distribution grid, dead ends, ageing water mains, distribution loops, points with the potential for cross connection/back flow and extremities of the distribution system. In some cases, secondary disinfection is delivered in the distribution system (i.e. at a chlorine booster station). Samples should also be collected immediately after this secondary disinfection is delivered.

The objective is to measure the quality of water being supplied to the consumer. Whenever possible samples should be taken at dedicated sampling stations within the distribution system. These stations should eliminate the effects of residential plumbing. If residences are used, cold water taps where drinking water is consumed should be sampled to eliminate the effects of deposits in the hot water tank. Samples must be taken prior to water softeners or other home-treatment devices, and should preferably be taken from taps located on a service pipe connected directly to the water main. Local plumbing problems such as line-breaches or illegal connection to cisterns that allow the entry of water that has not been disinfected into the system must be avoided. Sample taps that are used infrequently should be avoided as localised microbial growth and mineral crusts within the plumbing fixtures may affect the sample. Similarly, lines in which water pressure is not constant should be avoided

because temporary changes in line pressure may break up and suspend biological growth and metal crusts that may be attached to walls of the lines. Leaking taps and taps where water tends to run up the side of the lip of the faucet should not be used.

3.4 Sample Containers

Sampling containers are usually provided by the laboratory that is conducting the testing. Generally, plastic or glass containers are recommended for inorganic and microbiological tests but most tests for organic compounds require glass bottles. Exceptions to the use of glass for organic compounds may include tests for the measurement of diquat, paraquat and glyphosate. If in doubt, the sample should be collected in a glass container. Amber glass containers are recommended for organic compounds that are light-sensitive. If this is not possible, the container should be wrapped in aluminum foil or kept stored in a light-proof case.

Certain tests have specific volume and container-cleaning requirements. Microbiology tests require aseptic containers and many organic tests require 1 litre sample volumes. Other methods, such as one used for the measurement of volatile organic compounds, accommodate analysis directly from the sampling container. For these methods, the laboratory may recommend vials with Teflon™ septum caps. A summary of the Ministry of the Environment's sampling containers and volume requirements for each regulated parameter is provided in Table 1. Further information on containers is provided in the section entitled Sample Collection. It is very important to use the sampling container recommended by the laboratory conducting the testing.

3.5 Sample Collection

The collection and handling of samples is crucial to obtaining valid data. Person(s) collecting regulatory samples should be properly trained, with respect to sample handling considerations, including aseptic procedures for the collection of samples for microbiological testing. Disposable gloves should be worn and care must be taken that the inside of the container and cap do not come into contact with anything other than the atmosphere. If the inside of the sampling container is touched, it must be considered contaminated and should not be used. While the sample is being taken, the exterior of the cap should be held in your fingertips.

The collection of drinking water grab samples is generally done from taps or spigots located at the sampling points. Sampling taps should be free of aerators, hose attachments, strainers and mixing type faucets. The best method for collecting a grab sample is to collect the sample directly into the container provided by the laboratory. This eliminates the potential for sample contamination through the use of an intermediate container. This is especially important for analytes that are usually present in trace amounts (e.g. some metals, pesticides, dioxins/furans etc.).

In some situations, such as when taps and spigots do not have enough clearance from the floor, it is not possible to collect the sample directly into the laboratory container. In these cases, it may be necessary to collect the sample in an intermediate vessel and subsequently transfer the sample to the laboratory container. Information on types and pre-cleaning methods for intermediate vessels is provided in the section, Intermediate Sampling Containers. Metal and plastic sampling equipment, other than tubing and the plumbing in place, should not come into contact with the collected samples. Teflon™ or stainless steel tubing is recommended for permanent sampling installations. **In the case of sampling for microbiological testing, phenols, sulphide, volatile organic compounds, hydrocarbons, and oil and grease (not regulated), the sample must always be collected directly into the laboratory sample container.**

Samplers should take care to avoid inadvertently contaminating the sample with the target analyte. This can occur in instances where the sample comes into contact with an unsuitable preservative that is not required to stabilise the analyte in the sample. Common examples include: potassium dichromate preservative causing chromium contamination in samples taken for metals analysis; residual nitric acid preservative on hands or gloves causing nitrate contamination in samples taken for nitrate analysis; or sodium thiosulphate preservative causing sodium contamination in samples taken for cation measurements.

Some sample containers are pre-charged with preservative; field personnel must avoid rinsing containers prior to sample collection. Also, sample containers for organic compound analysis should never be rinsed with the sample, as the organic compounds from the rinse may accumulate on the container walls and compromise the accuracy of the analytical results. Sample containers should be filled slowly to prevent overflowing when containers have been pre-charged with preservative, and to eliminate bubble formation. Specific sampling information for each regulated parameter in the Drinking-Water Systems Regulation is provided in Table 1. This table is based on the Ministry of the Environment's practices and methods and can be used as a guide.

The protocol for sample collection at communal wells sometimes requires purging of the well to achieve a stable pH and turbidity measurement, before sample collection. Purging is not required for communal wells in which the pump runs continually and where in-line plumbing is present. For these wells, flushing the lines for a minimum of two minutes prior to sample collection is sufficient. However, communal wells that are not currently used or that are used intermittently should be purged by flushing the lines with a volume of water equivalent to three to five times the volume of water standing in the well. (The volume will depend on the static level and the inside diameter of the well casing). For pumps that are operated intermittently, the purge volume must be calculated with respect to length of use and the size of

storage/pressure tanks. If storage tanks are present, an adequate volume must be purged to ensure that the volume of water in the tank is completely exchanged.

In terms of chemistry, the U.S. EPA recommends purging a well until pH and turbidity measurements stabilise and turbidity is less than 10 NTU. For new, recently installed wells, purging is necessary to eliminate the effects of well installation. This document assumes that in-place plumbing and dedicated pumps can be used to facilitate purging. When this is not the case purging must be done with peristaltic, centrifugal or submersible pumps or with bailers. Discussion of these techniques and precautions for using these techniques is beyond the scope of this document and the reader is referred to Reference 8 listed at the end of this document.

Samples in distribution systems must always be taken from a cold water tap. The lines should be flushed prior to sample collection to negate the effects of local residential plumbing. As a general practice, this can be achieved by flushing the system until the water reaches a constant temperature (usually between two and five minutes).

3.5.4 Specialized Sampling Techniques:

While sampling information based on Ministry of the Environment's methods of analysis is presented in Table 1, specialised sampling techniques for particular tests warrant further discussion.

Volatile Organic Compounds (VOCs)

Volatile organic compounds are, as their name suggests, volatile and are easily vaporised from the sample. For this reason, some methods allow for sample collection in vials with septum caps (Teflon™-lined silicone discs) which can be placed directly in the auto-sampler of the analytical instrument. This eliminates the sample transfer step, which could induce a loss of volatile compounds to the atmosphere. If vials are not available, a glass bottle may be substituted provided that correct sampling techniques are used.

Samples should be collected in duplicate. Some laboratories may require triplicate samples. Laboratories may also recommend the use of a travelling blank that is opened at the sampling location for the duration of the sampling period, then closed and returned to the laboratory with the samples. The laboratory will provide direction on the collection of replicate samples and the use of travelling blanks. Chlorinated water samples require a preservative to quench the reaction of sample analytes with any surplus chlorine, and thus keep the sample representative of the system at the time the sample was taken. The vials may be pre-charged with a sodium thiosulphate pellet or powder. If the containers are not pre-charged with sodium thiosulphate, two drops of 25% weight/volume sodium thiosulphate per 50 mL of sample should be added to the container first.

Aerators and strainers must be removed from taps during sample collection, and the water should be running slowly. Extreme caution must be taken to eliminate turbulence. The vials or bottles should be filled slowly to the top rim of the container so that a dome or convex meniscus is present. A slight loss of sample may occur when the cap is applied. When capped, the cap or septum should be in contact with the sample so that no air is trapped in the sample container and when the vial or bottle is turned upside down no air bubble is present.

Microbiological

Aseptic techniques must be followed when handling the sterile sample bottles used for microbiological sample collection. Failure to do so will compromise the results. Aerators, hose attachments, filters and strainers may harbour bacteria and should be removed from taps when sampling for microbiological parameters. In other words, there must be a clear pathway from the distribution line to the sample collection container.

Cold water taps must be used, as water stored in hot water heaters is exposed to environmental conditions not representative of the water being supplied by the drinking-water system. The lines must be flushed prior to sampling. When sampling distribution system taps, it is advisable not to sample from an unprotected outside tap. Samplers should be aware that if raw surface water samples are taken from the near shore area instead of at the intake location, or if samples have been pre-chlorinated, the analytical results will not reflect the true bacteria count present at the raw water intake.

As it is especially important that the sterile bottles remain closed until the time of sampling, it is recommended that sample bottles for microbiological testing have caps with tamper-proof seals. If the seal is broken the bottle should be discarded. Appropriate care should be taken to ensure that only the outer surface of the cap and the bottle is touched/handled. The inside of the cap should not be allowed to come into contact with anything other than the atmosphere and the sample. After the sample is taken the bottle should be recapped immediately. When filling the bottle, the sampler should hold the bottle near the base and fill to the shoulder. If the sample bottle contains sodium thiosulphate, the bottle should not be rinsed before taking the sample. The bottle should be filled leaving approximately one inch of headspace. At least 120 mL of sample must be collected. To preserve the sample from further bacterial growth the sample should be refrigerated until transported to the laboratory and shipped with an ice pack. Further detail is provided in the section Sample Storage and Transportation.

Oil and Grease (Immiscible Liquids)

Routine sampling for oil and grease are not required under the Drinking-Water Systems Regulation or in the approvals for drinking-water systems. It is mentioned here, however, because there are often occasions when problems (e.g., spills in surface waters close to water supply intakes) warrant sampling for oil and grease. Oil and grease will float on top of the water body or well and the sampler must take great care to ensure that the sample adequately addresses the presence of immiscible liquids. The best practice is to choose a sampling location in the area of greatest mixing to ensure that you collect a representative sample. The sample container should not be rinsed, as the hydrophobic nature of the oil and grease will cause it to coat the inside of the sampling container resulting in inflated results which are not representative of the water sampled.

3.6 Intermediate Sampling Equipment

Although not recommended, the use of an intermediate sampling vessel is sometimes necessary. If an intermediate sampling container is used, it is best to contact the laboratory ahead of time for direction on the suitability of the container. In general, the preparation of sampling vessels should include hot water, phosphate-free detergent and thorough rinsing with analyte-free (e.g. distilled-) water. When sampling for organic compounds, an additional step of solvent rinsing should be incorporated into the cleaning regime. A glass vessel is recommended for intermediate sampling to ensure that all tests (organic and inorganic) can be performed. If funnels or tubing are required, Teflon™ or stainless steel should be used, as these materials offer low friction surfaces that do not readily adsorb contaminants from water.

While it is recognised that pumps (e.g. well pumps, high and low lift pumps) form an integral part of a water system, it is recommended that auxiliary sampling pumps be avoided as they contain brass, plastic, rubber and other materials that can contaminate samples. Moreover, they contain pump oil that can sometimes infiltrate into the sample. This is an important consideration for trace organic compounds and metals analysis. If auxiliary sampling pumps must be used, the reader is recommended to consult reference 8 listed at the end of this document.

3.7 Sample Filtering

Drinking-water samples should not be filtered in the field or at the laboratory prior to analysis. As it is not expected that the consumer filters their water prior to drinking it, unfiltered samples will provide a more representative sample of what the consumer is drinking. Unfiltered samples for the measurement of organic compounds and microbiological parameters are very important because many organic compounds adsorb to the particulate present in a water sample and membrane filtering will

remove bacteria from the sample. Filtering is not permitted in order to compensate for poor sampling technique or the use of inappropriate methods of analysis.

3.8 Sample Preservation

Preservation may be required to stabilise the analyte of interest in the sample prior to its transportation to the laboratory. The main types of preservation for drinking-water samples are refrigeration and pH control. Sample preservation requirements for the Ministry of the Environment's methods of analysis for regulated parameters are presented in Table 1.

Containers that have been pre-charged with preservative should not be rinsed or allowed to overflow or the preservative will be diluted. When strong acid or alkali is used to preserve a sample taken in plastic sampling containers, the preservative must be added after taking the sample. If the strong acid/alkali is added first, it may corrode the plastic container releasing contaminants to the sample. This is an important consideration in the preservation of samples with concentrated strong acid for trace metals analysis.

Preservatives should be stored separately to avoid cross contamination between preservatives, as this could result in inflated results for target analytes. An example of this is the contamination of nitric acid preservative by potassium dichromate preservative. When this occurs, the sample taken for metals analysis may show inflated results for chromium.

When preservatives are added to obtain a specific pH range, the sample should be swirled gently and left to equilibrate for two minutes. The pH should be checked with pH paper to ensure that the desired pH is reached. Different types of waters have different capacities for buffering (resisting a change in pH). The amount of preservative recommended in Table 1 is based on the majority of samples and should be used as a guide. It is recommended that the volume of preservative not exceed 1% of the sample. If this occurs, a note to this effect should be made on the sampling container label.

Refrigeration is also a form of preservation and is important to minimise chemical reactions and microbial growth in a sample. However, freezing a sample is not acceptable for some tests. In the case of microbiological testing, samples cannot be analysed if they have been frozen. It is very important that samples for these tests are shipped to the laboratory as soon as possible after collection.

3.9 Sample Holding Times

For certain tests, the sample must be received at the laboratory and analysed within a short period of time. Examples of perishable parameters include turbidity, microbiological contaminants, volatile organic compounds and N-nitrosodimethylamine. Table 1 lists suggested holding times for parameters listed in Schedules 1 and 2 of the Drinking-Water Quality Standards Regulation (O. Reg. 169/03), as well as parameters sometimes identified in approvals, control orders or other directives issued by the Ministry of the Environment. These holding times are based on Ministry of the Environment's methods of analysis.

Preservation stabilises the sample to differing degrees. For example, in the case of metals preservation may extend the allowable storage time to weeks or even months. However, some reactions (e.g. changes in nitrogenous compounds) continue unabated and preservation to prevent these reactions without compromising the sample is not possible. Consequently, refrigeration and transportation of all drinking water samples to the laboratory immediately after collection is encouraged to ensure that samples may be analysed within the appropriate time frames.

3.10 Sample Labelling

Accurate and complete labelling of samples ensures that the sample's identity is maintained. This is very important for sample tracking and data interpretation and is mandatory for sample data reporting and adverse water quality notification requirements under the Drinking-Water Systems Regulation (O. Reg. 170/03). It is advisable to pre-label all sample containers prior to taking the sample or to label each container **immediately** after the sample is taken to prevent confusion. An indelible marker or pen should be used and the material from which the label is comprised should be able to withstand water. In most cases, the laboratory conducting the analysis will supply the sampling container. Sample containers may have labels affixed to the container itself; alternatively the label or sample tag may be provided separately and attached to the container after the sample is collected. If the tags/labels are separate, the sampler should attach them prior to or immediately after taking the sample to prevent incorrect labelling.

When sample tags/labels are separate, a pre-printed sample identification number/code on the label may be available. This assigns a unique identification number/code to the sample in the field. If a pre-printed sample number is not assigned, it may be necessary for the sampler to create a field sample number. The sample ID generated should be simple and unique to the sampling set/batch collected. The following information should be recorded on either the sample label or on an accompanying sample information sheet.

1. Marking to indicate that this is a *regulated drinking-water sample*.

2. Sample type: raw, treated or distribution
3. A unique sample identifier
4. The legal name of the water system (available in DWIS).
5. The waterworks number, if applicable
6. The date and time of sample collection
7. The street address, if the sample is a distribution sample
8. Preservative(s) used.
9. Pertinent field measurements (Cl residual, turbidity, pH) (if room on the label/tag permits).
10. The initials of the sampler.

Much of this information can be put on the labels/tags in advance of sampling, either by the laboratory or the sampler. Pre-printed labels with the drinking-water system name, number, sample type, etc., are convenient, provide the necessary information for the lab analyst and help prevent mix-ups in labelling. In some cases sample tags used by laboratories have space to write the test requests. In other cases, a separate sample information sheet is used for this purpose and submitted to the laboratory with the samples.

If a separate sheet is used, some of the information need only be recorded on the sample information sheet. However, the sampler must ensure that information provided on the information sheet corresponds to information recorded on the sample bottle so that the laboratory staff can quickly match the information with the appropriate sample. The recorded sheet should also have the sampler's initials. Correctly recording the sample identification is especially critical in the face of human health implications and in the event that a sample must be traceable for litigation purposes. Correct sample identification is also the key to ensuring the accurate reporting of adverse water quality results for regulatory purposes.

The rapid identification of samples at the laboratory helps to ensure that samples are analysed promptly and that adverse water quality in treated and distribution drinking-water samples are immediately reported. The Ministry of the Environment affixes green labels bearing the words *Drinking-Water Regulation Sample* to facilitate this rapid sample recognition. Laboratories testing drinking-water samples should have a similar system in place to quickly cull these samples. Information on how to obtain these stickers is available from the Ministry of the Environment's Laboratory Services Branch Help Desk at (416) 235-6030.

3.11 Sample Storage and Transportation

It is recommended that all samples be delivered to the laboratory as soon as possible after sampling. Samples should be kept cool (refrigerated) if immediate shipping is not possible. Samples should be packaged to avoid breakage during shipping. Samples

must be shipped to arrive at the laboratory before the holding time for the samples has expired.

Samples for microbiological testing should be packed with ice packs or a suitable leak-proof container of ice and shipped in insulated boxes/coolers. Packing the sample with loose ice is not recommended as it may contaminate the sample. The ice should be encased in waterproof packaging or a sealed container. Optimal temperatures conditions during transport are less than 10°C. The inclusion of maximum/minimum thermometers beside the sample(s) during shipment may provide further information on sample conditions during transport and may help to validate the integrity of the sample.

Although samples must be cool, it is important to ensure that samples for microbiological testing do not freeze during shipment. Some courier companies offer shipping in heated vehicles during the winter months.

The sample container should be sealed for shipping. Doing so will help make obvious any evidence of tampering. This may simply involve the use of a label or similar item that must be torn to open the box/case. The sample information sheet, if used, and the chain-of-custody record must be included in the shipping box/case. A written record of how the samples are shipped, the time, date, carrier and tracking numbers for the shipments should be kept by the sampler.

The laboratory generally provides instructions for sample delivery to the laboratory. If samples are shipped directly by bus, train or air without the use of a courier, the sampler should notify the laboratory and provide flight/bus numbers, expected arrival times, way bill numbers, etc. to ensure that the laboratory arranges sample pick-up from the airport or bus/train terminal.

Sample storage conditions at the laboratory should be secure and should inhibit sample degradation or chemical/biological changes to target analytes prior to analysis.

4.0 Chain Of Custody

As previously mentioned, proper sample labelling is crucial to maintaining the identity of a sample. However, additional measures are then required to ensure a sample is traceable from the time of collection through to its analysis. These steps are referred to as a *chain-of-custody* and are used to ensure the integrity of the sample and resulting data. A sample or set of samples is considered to be "in custody" if it is in a custodian's physical possession or view, if it was in the custodian's physical possession and was then secured to prevent tampering, or if it is placed in a secured area. When samples are taken for litigation purposes, a chain-of-custody form provides an accurate written record that can be used to trace the possession, transfer

and custody of a sample from the time of its collection through to its introduction into the analytical data set. Each person involved in the chain of possession must sign the custody form when a sample or set of samples is received or relinquished.

In the case of drinking water samples, a chain-of-custody form must accompany samples to the point of receipt by the laboratory. The intent of this form is to document the transfer of custody of the samples from the sample custodian (sampler) to any other person and to the laboratory. It is recommended that the fewest number of people as possible be responsible for sample collection and transfer to the laboratory. If common carriers are used, receipts should be kept and, if packages are mailed, they should be registered and return receipts requested. These should be kept as part of the chain-of-custody documentation.

Once the samples have arrived at the laboratory, the chain-of-custody form must be signed off by an authorised person at the laboratory receiving the samples. The custodian should note either on the chain-of-custody form or on the sample information sheet provided with the samples, any samples that arrive in a condition unsuitable for analysis (e.g., broken, improperly preserved). This includes checking sampling dates recorded on containers and information sheets to make certain that holding times for the tests requested have not been exceeded. Samplers should be notified immediately of samples that cannot be analysed so that a second sample can be taken. The laboratory staff should record the time and date that the sampler was contacted. It is not necessary that the chain-of-custody document accompany routine (non-litigation) drinking water samples to each analytical department as long as an electronic or hardcopy record of sample routing within the laboratory is maintained. This will ensure a traceable chain of possession.

Laboratories, drinking-water system owners/operators and Ministry of Environment Provincial Officers having access to the Drinking Water Information System (DWIS), may obtain a chain-of-custody form from DWIS. The URL for DWIS is http://www.ene.gov.on.ca/environet/dwis/index.htm. This form can be retrieved from the Drinking Water Information System by the laboratory conducting the tests, customised for the drinking-water system and sent to the sampler with the sampling containers. The laboratory may already have its own chain-of-custody form and this is acceptable as long as similar information is tracked.

Laboratory staff must check that the information provided on the sample container tag/label matches information recorded on other sample information sheets and/or chain-of-custody documents. Samples should be handled and managed within a secure environment Temporary sample storage must be in a place that is clean, dry, lockable and environmentally-controlled to prevent analyte degradation prior to analysis. A record must be made of the date of analysis and the name of the analyst.

The sample must be in the analyst's possession or view, or secured in an area accessible only to authorised personnel at all times while in the laboratory.

Samples may be discarded when sample holding times have expired, if the sample has deteriorated for other reasons or is exhausted, if the results have been approved and released to the customer or if it is certain that no further information is required (e.g., repeat analysis). Records of sample destruction should be kept.

5.0 Summary

Continual verification that safe drinking water is supplied to the public can only be done when monitoring locations adequately represent all aspects of the water supply and samples taken accurately reflect the physical, chemical and biological attributes of the water sampled. Meeting both of the above conditions will result in the early detection and rapid resolution of water quality problems. The intent is for these recommended practices to be accompanied by analytical methods that are appropriate and fit for the purpose of analysing drinking water samples. The reader is referred to the Drinking-Water Testing Services Regulation (O. Reg. 248/03), and the companion document a *Protocol of Accepted Drinking Water Testing Methods*, Laboratory Services Branch, Ministry of the Environment, June, 2003 (as amended from time to time) for further information regarding suitability of methods of analysis.

It is the duty of both the sampler and the laboratory to ensure the implementation and continued use of best practices and accepted testing methods for the collection and analysis of drinking water samples. The quality of the data produced can only be as good as the poorest level of quality assurance in the entire process of sampling and analysis.

6.0 References

1. Ontario Ministry of the Environment (1993). A Guide to the Collection and Submission of Samples for Laboratory Analysis, Customer Services Unit, Laboratory Services Branch, December 1993.

2. Ontario Ministry of the Environment (2001). Laboratory Services Guide to the Submission of Samples for Laboratory Analysis.

3. Ontario Ministry of the Environment, Laboratory Services Branch (2003). Protocol of Accepted Drinking-Water Testing Methods. June 16, 2003

4. Ontario Regulation 170/03, Drinking-Water Systems Regulation, made under the *Safe Drinking Water Act,* June 2003.

5. Ontario Regulation 169/03, Drinking-Water Quality Standards Regulation, made under the *Safe Drinking Water Act,* June 2003.

6. Ontario Regulation 248/03, Drinking-Water Testing Services Regulation, made under the *Safe Drinking Water Act*, July 2003

7. United States Environmental Protection Agency (1997). *Manual for the Certification of Laboratories Analyzing Drinking Water – Criteria and Procedures Quality Assurance*. Office of Ground Water and Drinking Water, Cincinnati, OH. EPA 815-B-97-001.

8. United States Environmental Protection Agency (1996) (includes 1997 revisions). *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual*. U.S. Environmental Protection Agency, Athens, Georgia.

9. Ontario Clean Water Agency (2003). Standard Operating Procedures, (microbiological sampling and general chemistry sampling).

TABLE 1. Recommended Sampling Requirements, Based on Ministry of the Environment Test Methods for Drinking Water Samples

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Total Coliforms	Glass or plastic	250	30 mg Sodium thiosulphate	48 hours	5°C ± 3°C	Transport chilled, not frozen
Escherichia coli or fecal coliforms	Glass or plastic	250	30 mg Sodium thiosulphate	48 hours	5°C ± 3°C	Transport chilled, not frozen
Heterotrophic plate count or total coliform background count by membrane filtration	Glass or plastic	250	30 mg Sodium thiosulphate	48 hours	5°C ± 3°C	Transport chilled, not frozen

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Volatile Organics 1,1-dichloroethylene 1,2-dichlorobenzene 1,3-dichoroethane 1,4-dichlorobenzene benzene carbon tetrachloride dichloromethane ethylbenzene monochlorobenzene tetrachlorobenzene toluene trichloroethylene trihalomethanes: bromoform trihalomethanes: bromodichloromethane trihalomethanes: chloroform trihalomethanes: chlorodibromomethane vinyl chloride xylene – total xylene – ortho xylene - m/p	40 mL EPA-type glass vials with Teflon®-clad silicon rubber septa. Alternatively, 250 mL glass bottles with Teflon or foil lined screw caps. If bottles are used transfer must to vials must be done at the lab resulting in possible analyte loss (typically < 5%) and possible contamination from airborne contaminants	2 x 40	Sodium thiosulphate pill (10 mg) for chlorinated water or 2 drops per vial of 25% w/v sodium thiosulphate solution	14 days	Dark, 5°C ± 3°C	*Improper sample container, reversed cap liner, insufficient sample, headspace in the sample container will result an unsuitable sample for analysis.*

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Metals (except mercury) Aluminum Antimony Arsenic Selenium Barium Boron Cadmium Chromium Copper Iron Lead Manganese Selenium Uranium Zinc	Glass or plastic (PET)	50 but suggested sample size is 500 mL	Nitric acid to pH < 2 done immediately upon collection	60 days	Room temperature for preserved samples	Bottles with aluminum-lined caps are unacceptable

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Mercury	Glass	240	0.5-1.0 mL concentrated nitric acid (minimum 20 drops per 250 mL) and approximately 5 - 10 drops of potassium dichromate solution per 250 mL, pH must be < 2 and sample must be yellow colour	14 days	Room temperature for preserved samples	Unpreserved samples may be preserved at the laboratory, but a qualifier should be attached to the data
Nitrate Nitrite	Glass or plastic	10	None	7 days	5°C ± 3°C	Samples may be frozen
Triazene Herbicides: Atrazine Cyazine Metalachor Metribuzin Simazine Alachlor Prometryne	1 L amber glass bottles with Teflon™-lined screw caps	900	None	20 days to sample stabilisation	Dark 5°C ± 3°C	If insufficient volume of sample is received, the results should be reported with a corresponding increase in detection limits.

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Carbamate Pesticides: Bendiocarb Carbaryl Carbofuran Aldicarb Triallate	1 L amber glass bottles with Teflon™-lined screw caps	900	For chlorinated water add 1 mL of 25% w/v sodium thiosulphate solution	20 days to sample stabilisation	Dark 5°C ± 3°C	If insufficient volume of sample is received, the results should be reported with a corresponding increase in detection limits.
Organochlorine Pesticides and Total PCBs Trifluralin Aldrin + dieldrin Chlordanes (Total) Heptachlor + heptachlor epoxide Lindane DDT + metabolites p,p DDT DDT + metabolites o,p DDT Methoxychlor PCB (Total)	1 L amber glass bottles with Teflon™-lined screw caps	900	None	20 days to sample stabilisation	Dark 5°C ± 3°C	If insufficient volume of sample is received, the results should be reported with a corresponding increase in detection limits.

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Organophosphorus pesticides: Azinphos-methyl Chlorpyrifos Diazinon Dimethoate Malathion Parathion Phorate Terbufos Temephos	1 L amber glass bottles with Teflon™-lined screw caps	900	For chlorinated water add 1 mL of 25% w/v sodium thiosulphate solution	20 days to sample stabilisation	Dark 5°C ± 3°C	If insufficient volume of sample is received, the results should be reported with a corresponding increase in detection limits.
Phenoxyacetic acid herbicides and chlorophenols: 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) 2,4-dichlorophenoxyacetic acid (2,4-D) bromoxynil dicamba diclofop-methyl donoseb picloram 2,3,4,6-tetrachlorophenol 2,4,6-trichlorophenol 2,4-dichlorophenol pentachlorophenol	1 L amber glass bottles with Teflon™-lined screw caps	900	None	20 days to sample stabilisation	Dark 5°C ± 3°C	If insufficient volume of sample is received, the results should be reported with a corresponding increase in detection limits.

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Paraquat Diquat	500 mL high density polyethylene (PE) bottles	500	None	20 days to sample stabilisation	5°C ± 3°C	
Glyphosphate	500 mL high density polyethylene (PE) bottles	500	For chlorinated water add 1 mL of 25% w/v sodium thiosulphate solution	20 days to sample stabilisation	5°C ± 3°C	
Diuron	1 L amber glass bottles with Teflon™-lined screw caps	900	None	20 days to sample stabilisation	Dark 5°C ± 3°C	If insufficient volume of sample is received, the results should be reported with a corresponding increase in detection limits.
Fluoride	Polyethylene plastic	50	None	30 days	5°C ± 3°C	
Turbidity	Glass or plastic	50	None	7 days	Dark 5°C ± 3°C	Avoid freezing

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Benzo(a)pyrene	1 L amber glass bottles with Teflon™-lined screw caps	900	For chlorinated water add 1 mL of 25% w/v sodium thiosulphate solution	20 days to sample stabilisation	Dark 5°C ± 3°C	If insufficient volume of sample is received, the results should be reported with a corresponding increase in detection limits.
Cyanide (free)	Glass or plastic	500	Sodium hydroxide to pH ≦ 12	30 days for preserved samples	Room temperature for preserved samples	
Dioxins and furans (TEQ)	1 L amber glass bottles with Teflon™-lined screw caps	2 L preferable but 1 L may suffice	none	30 days	5°C ± 3°C	Keep cool during shipment (8ºC or less)
Nitrilotriacetic acid (NTA)	Plastic (PET)	50	None	30 days	5°C ± 3°C	

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
N-nitrosodimethylamine	1 L amber glass bottles with Teflon™-lined caps		None	10 days unless NDMA precursors are present or suspected in which case sample holding time is 2 days	Dark 5°C ± 3°C	If non-amber bottles are used protect samples from light by wrapping in aluminum foil or place in a light-proof container
Bromate	Plastic (PET)	50	See comments	28 days	5°C ± 3°C	Upon receipt a the lab, the sample should be sparged with N, He or Ar for 10 minutes and ethylenediamine preservative should be added to a concentration of 50 mg/L
Other Parameters Which May be Listed in Approvals and Orders (including OWRA orders)						
Alkalinity, pH	Plastic (PET)	100		14 days	5°C ± 3°C	
Chloride	Plastic (PET)	50		30 days	5°C ± 3°C	
Colour	Plastic (PET)	50		7 days	5°C ± 3°C	

Parameter/Test Group	Sample Container	Minimum Volume (mL)	Preservative	Maximum Holding Time	Storage Conditions	Comments
Dissolved Organic Carbon	Glass	50		14 days	5°C ± 3°C	
Sulphate	Plastic (PET)	50		30 days	5°C ± 3°C	
Sulphide	Glass	250	2 mL zinc acetate per litre followed by the dropwise addition and mixing of 5% sodium carbonate solution until precipitation is complete.	30 days	5°C ± 3°C	
Sodium	Plastic (PET)	50 but suggested sample size is 500 mL		30 days	5°C ± 3°C	
Total Dissolved Solids	Plastic (PET)	500		7 days	5°C ± 3°C	The solids test should be performed as soon as possible for the best result